Carboxylic acid functionalized ionic liquids as solvents for the recycling of rare earths

Bieke Onghena,[a*] Koen Binnemans[a]

[a] KU Leuven, Department of Chemistry, Celestijnenlaan 200F – P.O. box 2404, 3001 Heverlee, Belgium. Email: bieke.onghena@chem.kuleuven.be

During the Rare Earth Crisis in 2011, research on rare-earth elements was booming and research groups from all over the Western World were trying to secure the supply of rare earths by exploring the possibilities for the recycling of these scarce metals. Different recycling routes were constructed to extract rare earths from both End-of-Life consumer goods and industrial residues.[1,2]

Currently, ionic liquids (ILs) are intensively studied as environmentally friendlier alternatives for organic solvents in metal processing and hydrometallurgy. Ionic liquids are defined as liquids that consist entirely of ions and they are typically organic salts with a melting point below 100 °C. Because of their ionic character, ionic liquids generally have a negligible vapor pressure, low volatility and low flammability.

In our work, we are investigating the use of carboxylic acid functionalized ammonium and phosponium ionic liquids for the extraction and separation of rare-earth ions from acidic solutions. The cation is typically a quaternary phosphonium or ammonium, which is functionalized with a carboxyl group. The anionic part of the ionic liquid consists of an inorganic or fluorine-free organic anion, such as Cl^- or $CH_3SO_3^-$ (Figure 1). This novel type of ionic liquid extractants was applied to the recycling of rare earths from both End-of-Life consumer goods, namely NdFeB magnets, and industrial process residues, more particularly bauxite residue (red mud).[3] Due to the presence of a positive formal charge near the carboxyl function in the structure, this type of ionic liquid extractants is generally characterized by a higher acidity than similar traditional carboxylic acid extractants. This is advantageous for the extraction of rare-earth ions since in this way optimal extraction is obtained at pH values below the hydrolysis range of the rare earths, which is often not the case in traditional carboxylic acid systems. Furthermore, these systems could be considered to combine the properties of acidic and neutral extractants. Upon extraction, the acidic proton of the carboxyl is exchanged for coordination to the metal ion, which is typical for acidic extractants. However, by deprotonation, a zwitterion is formed which coordinates to the metal ion as a neutral ligand, similarly to neutral extractants.

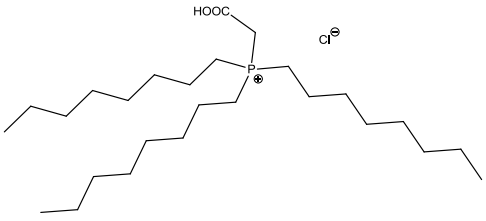

Figure 1. Example of a carboxylic acid functionalized phosphonium ionic liquid: (1-carboxyl)methyl trioctyl phosphonium chloride, $[P_{888}C_1COOH][Cl]$.

1 Binnemans K., Jones P.T., Blanpain B., Van Gerven T., Yang Y., Walton A., Buchert M. *Journal of Cleaner Production*, 2013, *51*, 1-22.
2 Binnemans K., Jones P.T., Blanpain B., Van Gerven T., Pontikes Y. *Journal of Cleaner Production*, 2015, in press, DOI 10.1016/j.jclepro.2015.02.089.
3 Onghena B., Binnemans K. *Industrial & Engineering Chemistry Research*, 2015, *54*, 1887-1898.